

696,680

(FILE 'HOME' ENTERED AT 11:49:05 ON 16 NOV 2004)

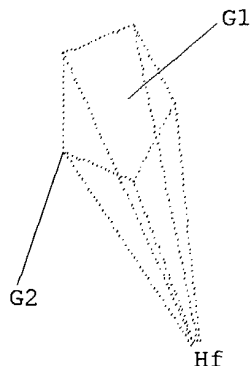
FILE 'REGISTRY' ENTERED AT 11:49:26 ON 16 NOV 2004

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



G1 n-Pr, i-Pr, n-Bu, i-Bu, s-Bu

G2 C, N, P, Si, Ge

Structure attributes must be viewed using STN Express query preparation.

=> s l1

SAMPLE SEARCH INITIATED 11:50:01 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 65 TO ITERATE

100.0% PROCESSED 65 ITERATIONS

1 ANSWERS

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*

BATCH \*\*COMPLETE\*\*

PROJECTED ITERATIONS: 817 TO 1783

PROJECTED ANSWERS: 1 TO 80

L2 1 SEA SSS SAM L1

=> s l1 full

FULL SEARCH INITIATED 11:50:08 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 1434 TO ITERATE

100.0% PROCESSED 1434 ITERATIONS

12 ANSWERS

SEARCH TIME: 00.00.01

L3 12 SEA SSS FUL L1

=> fil caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

155.42

155.63

FILE 'CAPLUS' ENTERED AT 11:50:14 ON 16 NOV 2004

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FILE COVERS 1907 - 16 Nov 2004 VOL 141 ISS 21  
FILE LAST UPDATED: 15 Nov 2004 (20041115/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s 13  
L4 17 L3

=> d 1-17 bib abs

L4 ANSWER 1 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2002:717700 CAPLUS  
DN 138:24987  
TI Copolymerization of ethene and propene in the presence of Cs symmetric group 4 metallocenes and methylaluminoxane  
AU Longo, Pasquale; Siani, Ermelinda; Pragliola, Stefania; Monaco, Guglielmo  
CS Dipartimento di Chimica, Universita di Salerno, Salerno, I-84081, Italy  
SO Journal of Polymer Science, Part A: Polymer Chemistry (2002), 40(19), 3249-3255  
CODEN: JPACEC; ISSN: 0887-624X  
PB John Wiley & Sons, Inc.  
DT Journal  
LA English  
AB Ethene-propene copolymns. were performed in the presence of Cs sym. group 4 metallocenes. The reactivity ratios were strongly influenced by both the transition metal and the ancillary ligands. Substantially alternate, almost random, and blocky copolymers were obtained with titanocene, zirconocene, and hafnocene, resp., with the bis(dimethylsilyl)-1,1'-2,2'-diyl-(3',5'-diisopropyl)(4-iso-Pr)-(cyclopentadienyl) ligand, and a blocky copolymer was obtained with (di-Ph methylidene)(cyclopentadienyl)(9-fluorenyl)TiCl<sub>2</sub>.  
RE.CNT 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN  
AN 2002:591964 CAPLUS  
DN 137:140917  
TI Transition metal compounds, polymerization catalysts containing them, propylene polymers, their compositions, and their moldings with excellent flexibility and transparency  
IN Minami, Hiroshi; Okamoto, Takaji  
PA Idemitsu Petrochemical Co., Ltd., Japan  
SO Jpn. Kokai Tokkyo Koho, 17 pp.  
CODEN: JKXXAF  
DT Patent  
LA Japanese  
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2002220414	A2	20020809	JP 2001-16595	20010125
PRAI	JP 2001-16595		20010125		
OS	MARPAT 137:140917				
AB	The polymers, useful for food and pharmaceutical packaging, show racemic pentad fraction (rrrr) 20-80 mol%, Mw/Mn $\leq 4$ , and Mw 100,000-1,000,000. Thus, propylene was polymerized in the presence of (iso-Bu) <sub>3</sub> Al, methylaluminoxane, and (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3,5-diisopropylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)hafnium dichloride and molded into a test piece showing tensile strength 30 MPa and haze 5%.				

L4 ANSWER 3 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2001:681428 CAPLUS  
 DN 135:227988  
 TI Propylene polymer calender-molded products with smooth surface  
 IN Junge, Naonori; Minami, Hiroshi; Machida, Shuji  
 PA Idemitsu Petrochemical Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 14 pp.  
 CODEN: JKXXAF

DT Patent  
 LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001253913	A2	20010918	JP 2000-66349	20000310
PRAI	JP 2000-66349		20000310		
AB	The moldings are manufactured from propylene polymers satisfying the relationships of $MIa/MIb \geq 0.240 + Mw/Mn + 3.1$ and $\log MS \geq 3.17 + \log \eta - 0.68$ [ $MIa$ (g/10 min) = melt index at 230°, 49-N load; $MIb$ (g/10 min) = melt index at 230°, 21.2-N load; $MS$ (g) = melt tension at 230°; $\eta$ = intrinsic viscosity at 135° in tetralin = 1.0-4.0 dL/g]. Thus, branched polypropylene [manufactured in the presence of dimethylsilylenebis(2-methyl-4-phenylindenyl)hafnium dichloride, branching by macromers; $\eta$ 2.3 dL/g, $Ma$ 2.8 g/10 min, $MIb$ 0.5 g/10 min, $Mw/Mn$ 2.5, $MS$ 0.60 g] was kneaded with additives and calender-molded to give a sheet showing elastic modulus 1630 MPa and uniform thickness.				

L4 ANSWER 4 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2001:680840 CAPLUS  
 DN 135:243319  
 TI Propylene polymer extrusion moldings with good surface properties  
 IN Junge, Naonori; Minami, Hiroshi; Machida, Shuji  
 PA Idemitsu Petrochemical Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 13 pp.  
 CODEN: JKXXAF

DT Patent  
 LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001253922	A2	20010918	JP 2000-66350	20000310
PRAI	JP 2000-66350		20000310		
AB	The moldings are manufactured from propylene polymers satisfying $MI49/MI21.2 \geq 0.240 + Mw/Mn + 3.1$ [ $MI49$ , $MI21.2$ = melt index at 230° under 49 N and 21.2 N load (g/10 min), resp.] and $\log MS \geq 3.17 + \log \eta - 0.68$ [ $MS$ = melt tension at 230° (g); $\eta$ = 0.5-2.5 = intrinsic viscosity at 135° measured in tetralin (dL/g)]. Thus, propylene was polymerized in the presence of methylaluminoxane and rac-dimethylsilylenebis(2-methyl-4-				

phenylindenyl)hafnium dichloride to give a polypropylene (MI49/MI21.2 = 5.2, Mw/Mn = 2.6, MS = 1.1,  $\eta$  = 800), which was made into a film.

L4 ANSWER 5 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2001:603626 CAPLUS

DN 135:181691

TI Propylene polymer foam products with uniform cells, thickness, and high expansion ratio

IN Junge, Naonori; Minami, Hiroshi; Machida, Shuji

PA Idemitsu Petrochemical Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 13 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001226512	A2	20010821	JP 2000-37615	20000216
PRAI	JP 2000-37615		20000216		

AB The products comprise propylene polymers showing intrinsic viscosity  $[\eta]$  0.5-3.5 dL/g and a specific relationship between MI49/MI21.2 (MI49, MI21.2 = melt index under 49 N and 21.2 N, resp.) and Mw/Mn, and between melt tension (MS) and  $[\eta]$ . Thus, propylene was polymerized in the presence of Al(Bu-iso)<sub>3</sub>, Me aluminoxane, and ( $\mu$ -dimethylsilylene)<sub>2</sub>(3,4-dimethylcyclopentadienyl)(3,5-diisopropylcyclopentadienyl)hafnium dichloride to give a macromonomer, which was polymerized with propylene using Al(Bu-iso)<sub>3</sub>, SiO<sub>2</sub>/Me aluminoxane, and dimethylsilylenebis(2-methyl-5,6-benzoindenyl)zirconium dichloride to give copolymer showing  $[\eta]$  2.0 dL/g, MI21.2 0.7 g/10 min, MI49 4.0 g/10 min, Mw/Mn 2.8, MS 6.3 g, and isotactic pentad fraction 93 mol%. A foam sheet was manufactured from the copolymer.

L4 ANSWER 6 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2001:603619 CAPLUS

DN 135:181686

TI Gel-free propylene polymer stretched films with good surface properties

IN Junge, Naonori; Minami, Hiroshi; Machida, Shuji

PA Idemitsu Petrochemical Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 12 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001226497	A2	20010821	JP 2000-37616	20000216
PRAI	JP 2000-37616		20000216		

AB Title films are made of propylene polymers satisfying the following relationships:  $MI5/MI21.2 \geq (0.240 + Mw/Mn) + 3.1$  [MI5 = melt index (g/10 min) at 230° 5.0 kg (49N) loading; MI21.2 = melt index (g/10 min) at 230° and 2.16 kg (21.2N) loading; Mw/Mn = (weight-average mol. weight)/(number-average mol. weight) by gel permeation chromatog.] and

logMS

$\geq 3.17 + \log[\eta] - 0.68$  [MS = melt tension (g) at 230°;  $[\eta]$  = intrinsic viscosity (dL/g) at 135° in tetralin;  $[\eta]$  = 1.0-3.0]. The films may contain other polyolefins. Thus, a biaxially stretched film mainly containing isotactic polypropylene [manufactured from polypropylene macromonomer and propylene in the presence of triisobutylaluminum, Me aluminoxane supported on silica, and dimethylsilylenebis(2-methyl-5,6-benzoindenyl)zirconium dichloride] showed good appearance.

L4 ANSWER 7 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2000:151501 CAPLUS

DN 132:194838

TI Manufacture of polyolefins with high molecular weight using metallocene catalysts

IN Imaeda, Kaori; Uehara, Yumito

PA Mitsubishi Chemical Industries Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 11 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2000072813	A2	20000307	JP 1998-241274	19980827
PRAI	JP 1998-241274		19980827		

OS MARPAT 132:194838

AB Polyolefins are manufactured by polymerization of  $\alpha$ -olefins in the presence of  $R_1m(CpR_2a)(CpR_3b)HfX_1X_2$  [ $R_1$  = bridging group containing Group 14 elements;  $Cp$  = cyclopentadienyl;  $R_2$ ,  $R_3$  = H, halo, Si-containing group, C1-20 (halogenated) hydrocarbyl, alkoxy, aryloxy, amino, with the proviso that when 2 of  $R_2$  and/or  $R_3$  are bonded to C atoms next to each other, they may form a ring;  $m = 0, 1$ ;  $a = b = 4$  if  $m = 0$ ,  $a = b = 5$  if  $m = 1$ ;  $X_1$ ,  $X_2$  = halo, H, C1-20 hydrocarbyl, alkoxy, aryloxy, amide, trifluoromethanesulfonic acid group] and ion-exchanged layered silicates. Thus, 1-butene and ethylene were polymerized in the presence of prepolymerized catalyst prepared from  $Cr^{3+}$ -exchanged synthetic mica, bis(n-butylcyclopentadienyl)hafnium dichloride,  $Et_3Al$ , and ethylene to give a copolymer with  $M_w 40.17 + 104$  and  $M_w/M_n 4.33$ .

L4 ANSWER 8 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1999:210500 CAPLUS

DN 130:352596

TI Group 4 Cs symmetric catalysts and 1-olefin polymerization

AU Grisi, Fabia; Longo, Pasquale; Zambelli, Adolfo; Ewen, John A.

CS Dipartimento di Chimica, Univ. di Salerno, Baronissi, I-84081, Italy

SO Journal of Molecular Catalysis A: Chemical (1999), 140(3), 225-233

CODEN: JMCCF2; ISSN: 1381-1169

PB Elsevier Science B.V.

DT Journal

LA English

AB Polymerization of propene and 1-butene promoted by group 4 Cs sym. metallocene precursors has been tested under different reaction conditions. The stereochem. structure of the polymer is affected by the radius of the transition metal, the substituent of the olefin and in some cases the reaction temperature and the monomer concentration. The results are tentatively rationalized considering the possible catalytic cycles that may produce either syndiotactic or isotactic polymers. A sample of syndiotactic polypropylene melting at  $170^\circ C$  is also reported.

RE.CNT 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 9 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1997:542473 CAPLUS

DN 127:206057

TI Supported metallocene catalyst systems for polymerization of ethylene

IN Agapio, Agapio K.; Litteer, Dwayne L.; Muhle, Michael E.

PA Exxon Chemical Patents Inc., USA

SO PCT Int. Appl., 37 pp.

CODEN: PIXXD2

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9729134	A1	19970814	WO 1997-US1839	19970207
	RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
	US 6090740	A	20000718	US 1997-788736	19970123
	EP 879250	A1	19981125	EP 1997-905774	19970207
	EP 879250	B1	20000920		
	R: DE, ES, FR, NL				
	ES 2151720	T3	20010101	ES 1997-905774	19970207
PRAI	US 1996-11330P	P	19960208		
	WO 1997-US1839	W	19970207		
OS	MARPAT 127:206057				
AB	<p>The title systems are prepared by combining porous supports, unbridged or achiral bridged metallocenes <math>Cp_mMR_nX_q</math> [<math>Cp</math> = (substituted)cyclopentadienyl group; <math>M</math> = Zr, Hf; <math>R</math> = halogen, H, alkyl; <math>m + n + q</math> = valence of <math>M</math>; <math>m \geq 1</math>; <math>n, q = 0-3</math>], and aluminoxanes (0.005-0.06 mmol transition metal/g support). The catalyst systems have improved metallocene loading and optionally reduced support particle size. A catalyst was produced from silica (Davison 952X), Me aluminoxane, and bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dichloride and was used in polymerization of ethylene and 1-hexene in isobutane.</p>				
L4	ANSWER 10 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN				
AN	1997:383272 CAPLUS				
DN	127:109009				
TI	Synthesis and characterization of trifluoro( $\eta^5$ -propyltetramethylcyclopentadienyl)metal(IV) compounds of the elements of Group IV				
AU	Kuenzel, Antje; Parisini, Emilio; Roesky, Herbert W.; Sheldrick, George M.				
CS	University of Goettingen, Institute of Inorganic Chemistry, Tammannstrasse 4, D-37077, Gottingen, Germany				
SO	Journal of Organometallic Chemistry (1997), 536/537(1-2), 177-180				
	CODEN: JORCAI; ISSN: 0022-328X				
PB	Elsevier				
DT	Journal				
LA	English				
AB	<p>A series of trifluoro metal complexes of titanium, zirconium and hafnium containing the propyltetramethylcyclopentadienyl ligand (<math>C_5Me_4Pr</math>) have been synthesized by metathesis reactions of the trichloro analog using 3 equivalent of <math>Me_3SnF</math>. X-ray anal. of <math>(C_5Me_4Pr)TiF_3</math> confirms the presence of two <math>(C_5Me_4Pr)TiF_3</math> moieties with two fluorine atoms bridging the metal atoms resulting in a center of symmetry. The starting materials <math>(C_5Me_4Pr)MCl_3</math> (<math>M</math> = Zr, Hf) were prepared by reaction of <math>(C_5Me_4Pr)Li</math> with <math>MCl_4</math> (<math>M</math> = Zr, Hf).</p>				
RE.CNT	8	THERE ARE 8 CITED REFERENCES AVAILABLE FOR THIS RECORD			
		ALL CITATIONS AVAILABLE IN THE RE FORMAT			
L4	ANSWER 11 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN				
AN	1997:240680 CAPLUS				
DN	126:225667				
TI	Stabilization of aluminoxane solutions by use of metallocenes				
IN	Agapiou, Agapios Kyriacos; Brant, Patrick				
PA	Exxon Chemical Patents Inc., USA				
SO	PCT Int. Appl., 18 pp.				
	CODEN: PIXXD2				
DT	Patent				
LA	English				
FAN.CNT	1				
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9706187	A1	19970220	WO 1996-US13067	19960809
	W: CA, JP				

RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

CA 2225493	AA	19970220	CA 1996-2225493	19960809
EP 843687	A1	19980527	EP 1996-928132	19960809
EP 843687	B1	20020612		
R: BE, DE, ES, FR, GB, IT, NL				
JP 11510546	T2	19990914	JP 1997-508695	19960809
EP 1153937	A2	20011114	EP 2001-116662	19960809
EP 1153937	A3	20021016		
R: BE, DE, ES, FR, GB, IT, NL				
ES 2178712	T3	20030101	ES 1996-928132	19960809
US 6180808	B1	20010130	US 1997-884426	19970627
US 6413900	B1	20020702	US 2000-716508	20001120
PRAI US 1995-513376	A	19950810		
EP 1996-928132	A3	19960809		
WO 1996-US13067	W	19960809		
US 1997-884426	A3	19970627		

OS MARPAT 126:225667

AB A method for stabilizing an aluminoxane solution comprises (1) combining a metallocene catalyst component with a solution of an aluminoxane and (2) aging the stabilized solution for time period of at least one month. A catalyst system for polymerizing olefins is obtained by combining the stabilized aluminoxane solution with addnl. amount of the metallocene.

L4 ANSWER 12 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1996:97134 CAPLUS

DN 124:146483

TI Method for producing silicon-bridged metallocene derivatives

IN Yoshizawa, Satoru; Matsukawa, Tetsuya; Ito, Seiju

PA Chisso Corp, Japan

SO Jpn. Kokai Tokkyo Koho, 24 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	JP 07252287	A2	19951003	JP 1994-42282	19940314
PRAI	JP 1994-42282		19940314		
OS	CASREACT 124:146483; MARPAT 124:146483				
GI					

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB The title compds. (I; R1 - R4 = H, C1-4 alkyl, trialkylsilyl, Ph; provided that at least one of R1 - R4 = H; M = transition metal; X = halo; v = 3-5), which are useful as homogeneous catalysts for polymerization of olefins, are prepared by coupling of 1,3-cyclopentadienes (II; R1 - R4 = same as above) with dimethyldihalosilane in the presence of a metal salt base R<sub>p</sub>YqM1 (R = C1-6 alkyl, Ph, H; Y = N, O, halo; p = 1-4; q = 0,1; M1 = alkali or alkaline earth metal) and a metal ion-sequestering agent to dimethylbis(substituted 1,3-cyclopentadienyl)silane (III; R1 - R4 = same as above) and dissolving the latter silane derivative in an ether solvent with addition of a strong base and reaction of the resulting product with a solution or a suspension of a transition metal halide MXv (M, X, v = same as above) in an ether solvent. Thus, 8.65 g 1,2,4-trimethylcyclopentadiene was dissolved in 200 mL (MeOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O and cooled in ice, followed by adding 56.8 mL 1.55 M BuLi/hexane over 0.5 h, and the resulting mixture was stirred at room temperature for 1 day to give a white suspension, to which was added a solution of 5.16 g dichlorodimethylsilane in 45 mL oxybis(methoxyethane) and

the resulting mixture was heated at 70-75° with stirring for 18 h to give, after vacuum distillation, the dimethylbis(substituted 1,3-cyclopentadienyl)silane III (R1 = R2 = R4 = Me, R3 = H) in 75% yield. The latter compound was dissolved in 150 mL THF, followed by adding 42.6 mL 1.55 M BuLi/hexane at -10° with stirring, and the resulting mixture was stirred at room temperature for 24 h to give a white suspension, which was added over 10 min to a suspension of 6.99 g ZrCl4 in 50 mL hexane and 350 mL THF at -78°, and the resulting mixture was slowly warmed to room temperature, stirred for 72 h, warmed to 65°, and stirred for 1 h to give 85.8 % the title metallocene (IV).

L4 ANSWER 13 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1992:425920 CAPLUS

DN 117:25920

TI Propylene oligomers

IN Watanabe, Masami; Ishihara, Nobuhide

PA Idemitsu Kosan Co., Ltd., Japan

SO Eur. Pat. Appl., 13 pp.

CODEN: EPXXDW

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 481480	A1	19920422	EP 1991-117740	19911017
	EP 481480	B1	19950125		
	R: BE, CH, DE, FR, GB, IT, LI, NL, SE				
	JP 05025215	A2	19930202	JP 1991-265191	19910917
	JP 3181945	B2	20010703		
	US 5171919	A	19921215	US 1991-777788	19911017
PRAI	JP 1990-278408	A	19901017		

OS CASREACT 117:25920; MARPAT 117:25920

AB Oligomerization of propylene in PhMe in the presence of triisobutylaluminum, ( $\eta^5$ -Me5C5)2HfMe2, [Et3NH][B(C6F5)4], and hydrogen gave 100 g 4-methyl-1-pentene, 7 g 2-methyl-1-pentene, 96 g trimer and 81 g tetramer.

L4 ANSWER 14 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1990:78185 CAPLUS

DN 112:78185

TI Manufacture of propylene oligomers with high selectivity and catalysts

IN Watanabe, Masami; Kuramoto, Masahiko; Tani, Noriyuki

PA Idemitsu Kosan Co., Ltd., Japan

SO Jpn. Kokai Tokyo Koho, 14 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 01207248	A2	19890821	JP 1987-287112	19871112
	JP 04057651	B4	19920914		
	JP 08109214	A2	19960430	JP 1993-214602	19930830
	JP 2732346	B2	19980330		
PRAI	JP 1986-270606		19861113		
	JP 1986-314436		19861225		
	JP 1987-50884		19870304		
	JP 1987-249364		19871002		

AB The title oligomers (d.p. mainly 2-10) are prepared by the polymerization of propylene and optionally other olefins in the presence of alkyl-substituted cyclopentadienyl zirconium and/or hafnium compds. and condensation products from organoaluminum compds. and water. Thus, 47.4



in mL AlMe<sub>3</sub> in toluene was treated with 35.5 g Cu<sub>2</sub>SO<sub>4</sub>·5H<sub>2</sub>O under Ar at 20° for 24 h, filtered from Cu<sub>2</sub>SO<sub>4</sub>, and concentrated to give 12.4 g Me aluminoxane (I) of mol. weight 721. Propylene (6 kg/cm<sup>2</sup> gage) was polymerized in the presence of 6 mmol I and 0.1 mmol bis(pentamethylcyclopentadienyl)zirconium at 55° for 4 h to give 30.3 g oligomer (average d.p. 4.6) containing dimer 4.7, trimer 1.8, and tetramer and higher 23.8 g. The dimer was mainly 4-methyl-1-pentene with selectivity 98%.

L4 ANSWER 15 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1989:594944 CAPLUS

DN 111:194944

TI Relative bond dissociation energies for early transition metal alkyl, aryl, alkynyl and hydride compounds. Equilibration of metalated cyclopentadienyl derivatives of peralkylated hafnocene and scandocene with hydrocarbons and dihydrogen

AU Bulls, A. Ray; Bercaw, John E.; Manriquez, Juan M.; Thompson, Mark E.

CS Div. Chem. Chem. Eng., California Inst. Technol., Pasadena, CA, 91125, USA

SO Polyhedron (1988), 7(16-17), 1409-28

CODEN: PLYHDE; ISSN: 0277-5387

DT Journal

LA English

AB Relative bond dissociation energies (BDEs) were obtained by equilibrating early transition metal alkyls and hydrides with H<sub>2</sub> or the C-H bonds of hydrocarbons. Thus, Cp<sub>2</sub>\*HfH<sub>2</sub> [Cp\* = (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>; C<sub>5</sub>H<sub>5</sub> = cyclopentadienyl)] equilibrates with Cp<sub>2</sub>\*HfPhH and dihydrogen in C<sub>6</sub>H<sub>6</sub>. From the enthalpy of the reaction, ΔH<sub>0</sub> = +6.0(3), the Hf-H BDE is calculated to be 0.8(3) kcal mol<sup>-1</sup> stronger than the Hf-C<sub>6</sub>H<sub>5</sub> BDE. Relative Sc-Ph and Sc-alkyl BDEs were estimated from the equilibration of the metalated complex Cp\*(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Sc, C<sub>6</sub>H<sub>6</sub> and Cp\*(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)ScC<sub>6</sub>H<sub>5</sub>, the Sc-C<sub>6</sub>H<sub>5</sub> BDE being 16.6(3) kcal mol<sup>-1</sup> stronger than the Sc-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub> BDE. From a similar reversible intramol. metalation of Cp\*(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>Pr)HfH<sub>2</sub> to give Cp\*(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)HfH and dihydrogen, the Hf-H BDE is estimated to be 23.0(3) kcal mol<sup>-1</sup> stronger than the Hf-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub> BDE. The equilibration of Cp\*(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>Ph)Sc-C.tplbond.CCMe<sub>3</sub> with metalated scandocene derivative Cp\*(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>)Sc and tert-butylacetylene lies very far toward Cp\*(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)Sc-C.tplbond.CCMe<sub>3</sub>, so that only a lower limit for the relative Sc-alkynyl and Sc-aryl BDEs may be determined: BDE(Sc-alkynyl)-BDE(Sc-aryl) ≥ 29(5) kcal mol<sup>-1</sup>. These early transition-metal-hydrocarbyl (M-R) BDEs correlate with the corresponding H-R BDEs (i.e., M-alkynyl > M-aryl > M-alkyl); however, the M-R BDEs increase more rapidly with s character for R than do the H-R BDEs. In order to probe the polarity of Sc-aryl bonds a series of scandocene derivs. capable of reversibly metalating at either of two differently substituted benzyl groups was prepared. The equilibrium consts. for these metalated derivs.: (η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>-o-C<sub>6</sub>H<sub>3</sub>-p-X)(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-m-CH<sub>3</sub>)Sc .dblarw. (η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-m-X)(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>-o-C<sub>6</sub>H<sub>3</sub>-p-Me)Sc (X = H, CF<sub>3</sub>, NMe<sub>2</sub>) were determined. The small dependence of K<sub>eq</sub> on the nature of X suggests that the Sc-aryl bond is essentially covalent with only a small ionic contribution.

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AN 1988:611618 CAPLUS

DN 109:211618

TI Organometallic catalysts and process for producing propylene oligomers

IN Watanabe, Masami; Kuramoto, Masahiko

PA Idemitsu Kosan Co., Ltd., Japan

SO Eur. Pat. Appl., 15 pp.

CODEN: EPXXDW

DT Patent

LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 268214	A1	19880525	EP 1987-116737	19871112
	EP 268214	B1	19910821		
	R: BE, CH, DE, FR, GB, IT, LI, NL, SE				
	US 4814540	A	19890321	US 1987-121507	19871113
PRAI	JP 1986-270606		19861113		
	JP 1986-314436		19861225		

OS MARPAT 109:211618

AB Propylene oligomers, useful as starting materials for polymers, and as base materials for preparing lubricating oils (no data), are prepared at high selectivity by oligomerizing propylene in the presence of a catalyst system comprising an alkyl-substituted cyclopentadienyl compound of Zr and/or Hf and a condensation product of an organoaluminum compound and water. Methylaluminoxane (prepared from Me<sub>3</sub>Al and CuSO<sub>4</sub>·5H<sub>2</sub>O) (mol. weight 721) was prepared, and 6 mmol was charged to an autoclave containing 400 mL PhMe, and then 0.01 mmol bis(pentamethylcyclopentadienyl)zirconium dichloride. The reactor was heated to 50°, and propylene continuously fed to the reactor at this temperature and 8 kg/cm<sup>2</sup>-gage for 4 h, producing 30.3 g propylene oligomers, consisting of dimer 4.7, trimer 1.8, and tetramer and higher oligomers 23.8 g. Anal. of the dimer showed that 4-methyl-1-pentene was the main component and was produced in 98% selectivity.

L4 ANSWER 17 OF 17 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1987:33235 CAPLUS

DN 106:33235

TI The tert-butyl peroxide complexes of permethylhafnocene, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Hf(R)(OOCMe<sub>3</sub>). Stoichiometric transformation of alkyl tert-butyl peroxide derivatives to alkoxy tert-butoxides, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Hf(OR)(OCMe<sub>3</sub>)

AU Van Asselt, Allan; Santarsiero, Bernard D.; Bercaw, John E.

CS Div. Chem. Chem. Eng., California Inst. Technol., Pasadena, CA, 91125, USA

SO Journal of the American Chemical Society (1986), 108(26), 8291-3

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 106:33235

AB Cp\*<sub>2</sub>Hf(R)(OOCMe<sub>3</sub>) (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>; R = Cl, H, Me, Et, Pr, Bu, CH<sub>2</sub>CHMe<sub>2</sub>, CH:CHCMe<sub>3</sub>, Ph, m-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and Cp\*(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Hf(OOCMe<sub>3</sub>) were synthesized and the crystal structure of Cp\*<sub>2</sub>Hf(OOCMe<sub>3</sub>)Et determined. Despite the coordinative unsatn. of the Hf center, the tert-Bu peroxide ligand is coordinated in a mono-hapto fashion. The mode of decomposition of these species is highly dependent on the substituent R. For R = H, Et, Pr, Bu, and CH<sub>2</sub>CHMe<sub>2</sub>, a clean first order conversion to Cp\*<sub>2</sub>Hf(OCMe<sub>3</sub>)(OR) was observed. These results are discussed in terms of a two step mechanism involving η<sup>2</sup>-coordination of the tert-Bu peroxide ligand. Homolytic O-O bond cleavage is observed upon heating Cp\*<sub>2</sub>Hf(OOCMe<sub>3</sub>)R (R = Ph, m-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). In the presence of excess 9,10-dihydroanthracene, Cp\*<sub>2</sub>Hf(OOCMe<sub>3</sub>)Ph gave Cp\*Hf(Ph)OH and HOCMe<sub>3</sub>. The O-O bond strength in these complexes was 22 kcal mol<sup>-1</sup>.